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(54) Title of Invention: A method for microwave synthesis of nanometer grade titanium carbide

(57) Abstract:

This invention involves a method for microwave synthesis of nanometer grade titanium carbide, in which titanium dioxide and acetylene carbon black are dried, and are then mixed even through ball-milling at the mass ratio of raw material : zirconium ball : absolute ethyl alcohol = 1 : 1 to 5 : 3 to 6, which is dried for implementation of synthesis through microwave heating. This invention makes use of microwave heating synthesis mainly based on the theory of carbothermic method, which is characterized by low reaction temperature, simple technological process and ease of control, and the condition of the TiC powder obtained does not promote conglobation, does not require reprocessing, and is free from impurities.

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Claims

1. This is a method for microwave synthesis of nanometer grade titanium carbide, and it has the following features: it includes the following procedures and technological conditions:
   Step One: dry titanium dioxide and acetylene carbon black to constant weight, and weigh materials at the mass ratio of titanium dioxide : acetylene carbon black = 80 : 36;
   Step Two: perform ball-milling for 12 to 24 hours at the mass ratio of raw material : zirconium ball : absolute ethyl alcohol = 1 : 1 to 5 : 3 to 6, till it is mixed even;
   Step Three: dry the slurry to constant weight;
   Step Four: heat to 1200 to 1400°C through microwave heating, and then hold it for 10 to 30 minutes at constant temperature.
2. With regard to the method for microwave synthesis of nanometer grade titanium carbide as mentioned in Claim 1, it has the following features: argon gas may be introduced as a protective gas in the process of microwave heating.

Description

A Method for Microwave Synthesis of Nanometer Grade Titanium Carbide

(I) Field of Technology

This invention involves the technological field of inorganic material, and specifically refers to a method for microwave synthesis of nanometer grade titanium carbide.

(II) Background Technology

Currently, the ordinary methods for titanium carbide (TiC) synthesis can be divided into three types: (1) use of metallic titanium or titanium halide for direct synthesis of TiC through carbonization; (2) use of gas titanium halide (for example: $TiCl_4$) for synthesis of TiC through pyrolysis in a carbon-containing atmosphere; (3) synthesis of TiC through carbon thermal reduction of TiO_2 under high temperature in a controlled atmosphere. The method for synthesis of TiC at relatively low cost is to produce it through TiO_2 reaction with carbon black at 1700 to 2100°C. The equation is:

$$TiO_2 + 3C = TiC + 2CO\uparrow$$

But the method is limited to a certain degree. Because the progress of reaction is under the influence of TiO_2 particle size and the degree of mutual contact, the synthetic product will contain TiO_2 and carbon black that have not reacted completely. In order to improve the contact surface between TiO_2 and C so that carbon black can be well distributed on the surface of TiO_2 particles, one of the methods is to decompose C_3H_6 gas at 400 to 600°C so that the C powder obtained after its decomposition can be evenly distributed on the surface of TiO_2 particles, and then TiC is synthesized through carbon thermal reduction of TiO_2 in the inert gas. High-quality TiC can be produced through this technological process. It has the following features: C powder can be evenly coated on TiO_2 particles; the contact area is large between C powder and TiO_2 particles; and the synthesized TiC is of fine particles (< 0.1 um).

When metallic Ti powder and C powder are used to synthesize TiC, it is mostly performed through self-propagating high temperature synthesis (SHS), but the use of SHS for synthesis of TiC will subject the purity thereof to the influence of the gases as contained in the reactant, such as water vapor, hydrogen gas, carbon dioxide and hydrocarbon. Therefore, before the reaction begins, the reactant shall be treated through vacuum baking at a proper temperature. In addition, a chemical coprecipitation *in-situ* synthesis process can also be used, and the reaction precursor for this process is in liquid state (such as titanium sulfate and butyl titanate), which is mixed with sucrose at the reaction ratio to prepare a buffer solution, and is then concentrated, dehydrated and carbonated at a certain temperature, and the temperature is thereafter increased to 1750°C in the protective atmosphere to synthesize TiC through carbonization. Currently, some people are also doing research work on preparation of TiC through reactive ball-milling technology.

A comprehensive view reveals that the existing technologies for preparation of TiC all have some disadvantages: the reaction temperature is high, and is above 1400°C in all cases; the preparation technology is complicated, and the technological process is relatively difficult to control; TiC prepared by SHS is lumpy, and needs ball-milling, and after that, the product can only reach micron grade, and may be mixed with all kinds of impurities in processing.

(III) Content of Invention

In order to overcome the defects in existing technologies, this invention provides a method for microwave synthesis of nanometer grade titanium carbide, which is simple in technological process, is easy to control, requires no reprocessing, is free from impurities, and can provide quick synthesis at relatively low temperature (1200°C).

This is a method for microwave synthesis of nanometer grade titanium carbide, and it has the following features: it includes the following procedures and technological conditions:

Step One: dry titanium dioxide and acetylene carbon black to constant weight, and weigh materials at the mass ratio of titanium dioxide : acetylene carbon black = 80 : 36;

Step Two: perform ball-milling for 12 to 24 hours at the mass ratio of raw material : zirconium ball : absolute ethyl alcohol = 1 : 1 to 5 : 3 to 6, till it is mixed even;

Step Three: dry the slurry to constant weight;

Step Four: heat to 1200 to 1400°C through microwave heating, and then hold it for 10 to 30 minutes at constant temperature.

Argon gas may be introduced as a protective gas in the process of microwave heating.

This invention mainly makes use of the theory of carbon thermal reduction, and the equation is:

$$TiO_2 + 3C = TiC + 2CO\uparrow$$

In comparison with the existing technologies, this invention has the following advantages and beneficial effects:

1. For this invention, CO gas is generated in reaction, and the pressure of CO will thus have an impact on the initial temperature for reaction, and based on reference, when Pco = 0.1 atm, the initial temperature for the abovementioned reaction is 1200°C. Because microwave heating is used to synthesize TiC, the temperature will reach 1200 to 1400°C quickly in the reaction, and quick synthesis of TiC can be implemented within the temperature range with synthesis rate at more than 97%. The crystal grain size for product TiC is 45.63 to 87.57 nm.

2. This invention is simple in technological process and easy to control, and the obtained TiC powder does readily conglobate, does not require reprocessing, and is free from impurities.

(IV) Specific Implementation Procedures

Implementation Case I:

Step One: in the oven, dry titanium dioxide (15 nm, rutile type, content > 91%) and acetylene carbon black (specific surface area 58.866 m^2/g), at 105°C, to constant weight, and weigh 87.7 grams of titanium dioxide and 36 grams of acetylene carbon black;

Step Two: take 450 grams of oxidized zirconium balls, 500 ml of 95% ethanol, and feed in raw material, and perform ball-milling and mixing for 12 hours in the aluminum oxide ball-milling tank (or rubber tank), till it is even;

Step Three: dry the slurry to constant weight at 100°C;

Step Four: weigh 75 grams of mixture and place it in the MFM-863 microwave sintering oven, then perform vacuum pumping for 20 minutes, introduce argon gas as a protective gas with pressure at 1 atm, heat to 1200°C through microwave heating, and hold it for 30 minutes at constant temperature.

Implementation Case II:

Step One: dry titanium dioxide (15 nm, rutile type, content > 91%) and acetylene carbon black (specific surface area 58.866 m^2/g) at 80°C in the oven to constant weight, and weigh 87.7 grams of titanium dioxide and 36 grams of acetylene carbon black;

Step Two: take 125 grams of oxidized zirconium balls, 300 ml of 95% ethanol, and feed in raw material, and perform ball-milling and mixing for 24 hours in the aluminum oxide ball-milling tank (or rubber tank), till it is even;

Step Three: dry the slurry to constant weight at 80°C;

Step Four: weigh 75 grams of mixture and place it in the MFM-863 microwave sintering oven, then perform vacuum pumping for 20 minutes, introduce argon gas as a protective gas with pressure at 1 atm, heat to 1300°C through microwave heating, and hold it for 20 minutes at constant temperature.

Implementation Case III:

Step One: dry titanium dioxide (15 nm, rutile type, content > 91%) and acetylene carbon black (specific surface area 58.866 m^2/g) at 90°C in the oven to constant weight, and weigh 87.7 grams of titanium dioxide and 36 grams of acetylene carbon black;

Step Two: take 620 grams of oxidized zirconium balls, 600 ml of 95% ethanol, and feed in raw material, and perform ball-milling and mixing for 18 hours in the aluminum oxide ball-milling tank (or rubber tank), till it is even;

Step Three: dry the slurry to constant weight at 90°C;

Step Four: weigh 75 grams of mixture and place it in the MFM-863 microwave sintering oven, then perform vacuum pumping for 20 minutes, introduce argon gas as a protective gas with pressure at 1 atm, heat to 1400°C through microwave heating, and hold it for 10 minutes at constant temperature.

For the three implementation cases as mentioned above, cool down to room temperature, discharge and weigh so as to calculate synthesis rate, then take a certain amount of TiC for performing phase analysis with X-ray diffraction and for performing particle size analysis with transmission electron microscope. Refer to the following table for results of analysis:

	Synthesis Rate%	Phase Analysis	Crystal Grain Size (nm)
Implementation Case I	97	97% of product is TiC, and the rest is TiO_2	45.63
Implementation Case II	100	Product is entirely TiC	87.57
Implementation Case III	100	Product is entirely TiC	59.04

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权利要求书1页 说明书4页 附图页数0页

[54]发明名称 一种微波合成纳米级碳化钛的方法

[57]摘要

本发明是一种微波合成纳米级碳化钛的方法，它是将二氧化钛和乙炔碳黑烘干后，按照料：锆球子：无水乙醇=1：1～5：3～6的质量比球磨混合均匀，烘干，微波加热合成。本发明主要是利用了碳热还原法原理，采用微波加热合成，反应温度低，工艺过程简单，易控制，所得TiC粉体不易团聚，无须再加工，无杂质。

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权　利　要　求　书

1.一种微波合成纳米级碳化钛的方法，其特征是，它包括如下步骤和工艺条件：

第一步　将纳米级二氧化钛和乙炔炭黑烘干至恒重，按照二氧化钛：乙炔炭黑＝80：36 的质量比称料；

第二步　按照料：锆球子：无水乙醇＝1：1～5：3～6 的质量比进行球磨混合 12～24 小时，至均匀；

第三步　将料浆烘干至恒重；

第四步　微波加热至 1200～1400℃后，恒温 10～30 分钟即可。

2.根据权利要求 1 所述的一种微波合成纳米级碳化钛的方法，其特征是，在微波加热时可以通入氩气做保护气体。

一种微波合成纳米级碳化钛的方法

（一）技术领域

本发明涉及无机材料技术领域，具体是指一种微波合成纳米级碳化钛的方法。

（二）背景技术

目前，一般合成碳化钛（TiC）的方法可以分成三类：（1）用金属钛或卤化钛直接碳化合成 TiC；（2）用气体卤化钛（如 $TiCl_4$）在含碳的气氛中热解合成 TiC；（3）在所控制的气氛中，高温下用碳碳热还原 TiO_2 合成 TiC。合成 TiC 较为廉价的方法是采用 TiO_2 与炭黑在 1700～2100℃反应制得。反应式为：

$$TiO_2 + 3C \xlongequal{} TiC + 2CO\uparrow$$

但该方法有一定的局限性。因为反应的进行程度受 TiO_2 颗粒大小及相互接触程度的影响，合成的产品中会含有未反应完全的 TiO_2 和炭黑。要改善 TiO_2 和 C 的接触面，使炭黑很好地分散在 TiO_2 颗粒表面，方法之一就是在 400～600℃分解 C_3H_6 气体，使其分解后得到的 C 粉均匀分布于 TiO_2 颗粒表面，然后在惰性气体中碳热还原 TiO_2 合成 TiC。这种工艺过程能够制备出高质量的 TiC。其特点是：C 粉能十分均匀地涂附在 TiO_2 颗粒上；C 粉与 TiO_2 颗粒的接触面积大；合成的 TiC 颗粒细（< 0.1um）。

用金属 Ti 粉与 C 粉合成 TiC，多采用自蔓延高温合成法（SHS），用 SHS 法合成 TiC，其纯度会受反应物中所含气体的影响，如水气，氢气，二氧化碳及碳氢化合物等。因此反应进行前，将反应物在适当的温度下真空焙烧处理。此外，还可以采用化学共沉淀原位合成法，这种方法反应前驱物为液态（如硫酸钛或钛酸丁脂），按反应比例与蔗糖混合配成一定的缓冲溶液，然后在一定的温度下，浓缩脱水碳化，然后在保护气氛下升温至 1750℃，碳化反应合成 TiC。目前，还有人探索用反应球磨技术制备 TiC。

综观这些制备 TiC 的现有技术，均存在一些不足之处：反应温度高，均在 1400℃以上；制备工艺复杂，工艺过程较难控制；SHS 法制备的 TiC 为

块状物，还需球磨加工，加工后只能达到微米级，还可能在加工过程中掺入各种杂质。

（三）发明内容

本发明就是为了克服现有技术中存在的缺陷，提供一种工艺过程简单、易控制、无须再加工、无杂质、能够在较低的温度下（1200℃）快速合成的微波合成纳米级碳化钛的方法。

一种微波合成纳米级碳化钛的方法，其特征是，它包括如下步骤和工艺条件：

第一步　将纳米级二氧化钛和乙炔炭黑烘干至恒重，按照二氧化钛：乙炔炭黑＝80：36 的质量比称料；

第二步　按照料：锆球子：无水乙醇＝1：1～5：3～6 的质量比进行球磨混合 12～24 小时，至均匀；

第三步　将料浆烘干至恒重；

第四步　微波加热至 1200～1400℃后，恒温 10～30 分钟即可。

在微波加热时可以通入氩气做保护气体。

本发明主要是利用了碳热还原法原理，其反应式为：

$$TiO_2 + 3C \xlongequal{} TiC + 2CO\uparrow$$

本发明与现有技术相比，具有如下优点和有益效果：

1.本发明在反应中有气体 CO 产生，故 CO 的压力会对该反应式的反应起始温度产生影响，根据参考文献，当 P_{CO}＝0.1atm 时，上述反应的起始温度为 1200℃。由于用微波加热合成 TiC，故反应很快达到 1200～1400℃，且能在该温度范围快速合成 TiC，合成率达 97%以上。产物 TiC 的晶粒大小为 45.63～87.57nm。

2.本发明工艺过程简单，易控制，所得 TiC 粉体不易团聚，无须再加工，无杂质。

（四）具体实施方式

实施例一

第一步　将二氧化钛（15nm，金红石型，含量＞91%）和乙炔炭黑（比表面积 58.866m^2 / g）在烘箱中 105℃烘干至恒重，称取二氧化钛 87.7 克、乙炔炭黑 36 克；

第二步　取氧化锆球子 450 克，95%乙醇 500ml，加料，在氧化铝球磨罐（或橡胶罐）中进行球磨混合 12 小时，至均匀；

第三步　将料浆在 100℃下烘干至恒重；

第四步　将混合料称 75 克装入 MFM-863 型微波烧结炉，然后抽真空 20 分钟，通入氩气作保护气体，压力为 1atm，微波加热至 1200℃，恒温 30 分钟即可。

实施例二

第一步　将二氧化钛（15nm，金红石型，含量＞91%）和乙炔炭黑（比表面积 58.866m^2 / g）在烘箱中 80℃烘干至恒重，称取二氧化钛 87.7 克、乙炔炭黑 36 克；

第二步　取氧化锆球子 125 克，95%乙醇 300ml，加料，在氧化铝球磨罐（或橡胶罐）中进行球磨混合 24 小时，至均匀；

第三步　将料浆在 80℃下烘干至恒重；

第四步　将混合料称 75 克装入 MFM-863 型微波烧结炉，然后抽真空 20 分钟，通入氩气作保护气体，压力为 1atm，微波加热至 1300℃，恒温 20 分钟即可。

实施例三

第一步　将二氧化钛（15nm，金红石型，含量＞91%）和乙炔炭黑（比表面积 58.866m^2 / g）在烘箱中 90℃烘干至恒重，称取二氧化钛 87.7 克、乙炔炭黑 36 克；

第二步　取氧化锆球子 620 克，95%乙醇 600ml，加料，在氧化铝球磨罐（或橡胶罐）中进行球磨混合 18 小时，至均匀；

第三步　将料浆在 90℃下烘干至恒重；

第四步　将混合料称 75 克装入 MFM-863 型微波烧结炉，然后抽真空 20 分钟，通入氩气作保护气体，压力为 1atm，微波加热至 1400℃，恒温 10 分钟即可。

上述三个实施例，冷却至室温后出料并称量，以计算合成率，然后取一定量的 TiC 用 X 射线衍射法进行物相分析，用透射电镜进行粒度分析）。分析结果见下表：

	合成率%	物相分析	晶粒大小（nm）
实施例一	97	产物97%为TiC，其余为TiO_2	45.63
实施例二	100	产物全为TiC	87.57
实施例三	100	产物全为TiC	59.04

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Affidavit of Accuracy

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